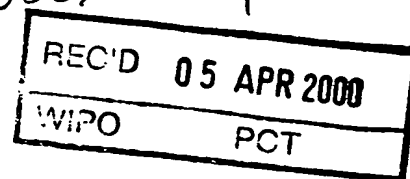




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I, KAY WARD, TEAM LEADER EXAMINATION SUPPORT AND SALES hereby certify that annexed is a true copy of the Provisional specification in connection with Application No. PP 9347 for a patent by SOUTHERN CROSS UNIVERSITY, LEIGH ALBERT SULLIVAN and DAVID MURRAY MCCONCHIE and RICHARD BUSH filed on 22 March 1999.

WITNESS my hand this  
Twenty-ninth day of March 2000

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**AUSTRALIA**  
*Patents Act 1990*

**PROVISIONAL SPECIFICATION**

**Invention Title:    APPARATUS FOR ANALYSING REDUCED INORGANIC  
SULFUR**

**This invention is described in the following statement:**

The present invention relates to an apparatus for the quantitative analysis of reduced inorganic sulfur.

Sulfur is present in the environment in several different forms which may be generally classified as organic and inorganic sulfur. The presence of each form of sulfur has important environmental implications. For example, combustion of both inorganic and organic sulfur produces sulfur dioxide, a greenhouse gas and source of acid rain. Another significant environmental problem is the acid generating potential of a class of inorganic sulfur materials known as reduced inorganic sulfur. These compounds produce acid when materials containing them are mined, excavated or drained.

The term "reduced inorganic sulfur" refers to sulfur in a form that can undergo oxidation and includes mineral disulfides (e.g. pyrite and chalcopyrite), monosulfides (e.g. sphalerite, galena and covellite), polysulphides (e.g. pyrrhotite and bornite), non-stoichiometric metal sulfides (e.g. greigite), other sulphides such as chalcocite, sulfites (salts of sulfurous acids) and elemental sulfur. In the present specification the term "reduced inorganic sulfur" will be understood to include any inorganic sulfur compound that can be oxidised.

Further types of naturally occurring inorganic sulfur compounds are the sulfate minerals, such as gypsum, which include sulfur in the oxidized sulfate form. These materials are generally not a source of acid in the environment.

When sulfide bearing material is mined or excavated, oxidation of the reduced inorganic sulfur may occur. The result is acid sulfate soil and acid mine drainage. Acid mine drainage refers to acid water produced by the oxidation of minerals such as pyrite in the presence of water and is one of the major environmental problems facing the mining industry. The oxidation of reduced inorganic sulfur in acid sulfate

soils is a global environmental problem affecting more than 12 million hectares of agricultural land worldwide, degrading aquatic habitats and corroding concrete and steel infrastructure. It is therefore important for environmental management to be able to measure the amount of reduced inorganic sulfur in a wide range of materials including sediments, soils, mine spoil, sludge, petroleum, mineral ores, fossil fuels and water.

There are several known methods for measuring the sulfur content of a material. Combustion followed by measurement of evolved sulfur oxides is used to measure the total sulfur content (i.e. the combined inorganic and organic sulfur). Such methods are typically used to measure the sulfur content of coal. Combustion of coal is a major source of sulfur dioxide pollution. However, the combustion method does not distinguish between organic sulfur, reduced inorganic sulfur or mineral sulfates and accordingly cannot be used to accurately quantify the reduced inorganic sulfur in a sample.

The most widely used method for assaying reduced inorganic sulfur is by peroxide oxidation in which the sulfur is oxidised to sulfate. The amount of sulfate liberated by peroxide oxidation is then analysed by conventional wet chemical quantitative analysis. Although this method is the accepted procedure, the present inventors have surprisingly and unexpectedly observed that the method is subject to serious interferences from organic sulfur and sulfate minerals such as gypsum. This interference is particularly important when sediments having low reduced inorganic sulfur are measured. An erroneous estimate of the reduced inorganic sulfur content may lead to the recommendation of costly and/or inappropriate and environmentally damaging management practices.

Other methods for analysing reduced inorganic sulfur, but which are considered to be less accurate than the peroxide oxidation method, include:

(a) measuring the total sulfur and soluble sulfur

content and estimating the reduced inorganic sulfur content from the difference between the two values. A disadvantage of such differential measurement is that the errors are cumulative.

- 5 (b) microscopic examination of a sample, and
- (c) indirect measurement by estimating the amount of pyritic iron ( $\text{FeS}_2$ ) in a sample. However non-pyritic forms of reduced inorganic sulfur are not measured.

10 It is therefore an object of the present invention to provide a method and apparatus for measuring the reduced inorganic sulfur content of a sample selectively and accurately.

According to a first broad form of the invention there is provided an apparatus for measuring  
15 the reduced inorganic sulfur content of a sample, the apparatus having a reaction chamber, means for introducing a reducing agent that can selectively convert the reduced inorganic sulfur of the sample in the reaction chamber to hydrogen sulfide and means for  
20 measuring the amount of hydrogen sulfide evolved by reaction of the reducing agent with the sample and means for detecting when evolution of the hydrogen sulfide has reduced or ceased.

The apparatus of the present invention has a  
25 reaction chamber for allowing a sample to be tested to be digested by a reducing agent that selectively converts the reduced inorganic sulfur component of a sample to  $\text{H}_2\text{S}$ . The reducing agent should not react with organic sulfur or sulfate materials to produce  $\text{H}_2\text{S}$ . Preferred reducing  
30 agents include chromous salts, stannous salts and mercurous salts.

An especially preferred reducing agent is acidified chromous chloride. Acidified chromous chloride solutions are typically prepared by passing acidified  
35 chromic chloride through a column containing zinc, pre-amalgamated in mercuric nitrate. This process is difficult, slow and requires specialised equipment to minimise atmospheric oxidation of the acidified  $\text{CrCl}_2$ .

Also, acidified  $\text{CrCl}_2$  is unstable and can only be stored for a few days. Thus, it is preferred that chromous chloride is generated in situ in the reaction chamber. Typically, chromium, concentrated  $\text{HCl}$ , ethanol and distilled water are introduced into the reaction vessel. The chromium is typically in the form of a powder, but may also be added as a pellet or slurry.

The reduction reaction is typically carried out in an inert atmosphere such as nitrogen or argon. Generally, the reaction is carried out at elevated temperatures with agitation under reflux conditions. In a particularly preferred embodiment of the invention, the apparatus includes a condenser that is cooled by means of a refrigerated coil instead of a conventional water cooled condenser. Typically the apparatus includes a heat exchange mechanism whereby the heat extracted by the coil is used to heat the reaction chamber. This arrangement minimises energy requirements and allows for the apparatus to be in the form of a portable unit which is suitable for use in the field.

The apparatus of the invention is typically automated and controlled by a central processor which can control some, or essentially all, of the functions of the apparatus. This allows the apparatus to be operated by non-skilled personnel.

Typically, the amounts of reagents added to the reaction chamber are automatically supplied to the reaction chamber in pre-determined quantities in a pre-determined order. Generally, the liquid ingredients are added using a peristaltic pump.

In a further broad form of the present invention there is provided an automated apparatus for measuring the reduced inorganic sulfur content of a sample, the apparatus having a reaction chamber, means for heating the chamber, a condenser, a refrigeration unit for cooling the condenser and which also provides heat to the heating means, means for introducing a reducing agent into the reaction chamber which converts

the reduced inorganic sulfur to hydrogen sulfide and measuring means for measuring the amount of hydrogen sulfide evolved.

5 The reduced inorganic sulfur composition of the sample may be calculated from the amount of  $H_2S$  evolved by reaction with the reductant. The  $H_2S$  evolution may be measured by any of the known methods of measuring  $H_2S$ . Such methods include colourimetric, turbidimetric and gravimetric methods. Particularly preferred methods  
10 include spectroscopic or chromatographic techniques such as mass spectroscopy, gas chromatography, UV or IR spectroscopy. A particularly preferred measurement means is an infra red gas analyser. Generally, the inert gas which provides the inert atmosphere in the reaction  
15 chamber also serves as a carrier gas to carry the evolved  $H_2S$  to the measurement means.

The amount of  $H_2S$  evolved may also be measured indirectly. For example,  $H_2S$  may be oxidised to sulfate or sulfur dioxide. These oxidation products may then be  
20 measured by suitable methods including turbidimetric or gravimetric, chromatographic or spectroscopic methods.

The apparatus of the present invention also includes a means for detecting when the evolution of  $H_2S$  has decreased to a pre-determined rate. Typically, this  
25 is when  $H_2S$  evolution has substantially ceased. Cessation of  $H_2S$  evolution indicates that the reduction reaction has been completed. When completed, a fresh sample may be analysed. With conventional wet chemical procedures, a sample is allowed to react for a pre-determined maximum  
30 length of time. The present inventors have observed that the reduction reaction can often take much less time than has traditionally been allowed. Thus, by being able to monitor when the reaction has ceased, sample throughput may be optimised.

35 The apparatus may include an alarm or other signalling device to alert an operator that the reaction has finished. Alternatively and/or in addition to, the apparatus may have means for automatically disengaging

any heating of the reaction chamber and deactivate the condenser on completion of the reduction reaction.

The means for detecting when evolution of  $H_2S$  has ceased may be in addition to, or part of, the  $H_2S$  measuring means. For example a gas sensor or other detection means may be associated with the reaction chamber to detect the  $H_2S$  therein. Gas sensors for detecting the presence of  $H_2S$  are known.

In the preferred embodiment where the  $H_2S$  measurement means is an IR gas analyser or other spectrophotometric analyser, the analyser may be programmed to detect when the rate of  $H_2S$  evolution has decreased.

Preferably the spectrophotometric analyser can measure the  $H_2S$  concentration on a real time basis to allow the rate of  $H_2S$  evolution to be constantly monitored. Typically, the  $H_2S$  evolution data may be represented as a function of cumulative  $H_2S$  concentration v time or absolute  $H_2S$  concentration v. time.

Different forms of reduced inorganic sulfur react at different rates. Thus, by being able to monitor the rate of  $H_2S$  evolution, information can be obtained as to the relative amounts of different forms of reduced sulfur materials present in the sample.

According to a further broad form of the invention there is provided an apparatus for measuring the amount of reduced inorganic sulfur in a sample, the apparatus having a reaction chamber, a means of introducing a reducing agent that can selectively convert the inorganic reduced sulfur of the sample in the reaction chamber to hydrogen sulfide and means for continually monitoring the amount of hydrogen sulfide evolved.

According to still a further broad form of the invention there is provided a method of measuring the amount of reduced inorganic sulfur in a sample, the method including reacting a sample with a reducing agent that selectively converts the reduced inorganic sulfur to



hydrogen sulfide and continuously monitoring the amount of hydrogen sulfide evolved.

The ability to determine the relative amounts of different types of reduced inorganic sulfur is important for environmental management. This enables predictions to be made as to the potential rate of acid generation as opposed to simply calculating the total acid generating potential of a soil material.

A knowledge of a form of sulfur generally referred to as acid volatile inorganic sulfur is of particular importance. Acid volatile sulfur includes monosulfides and non-stoichiometric sulphides such as greigite and mackinawite. In the preferred apparatus in which acidic chromous chloride is generated *in situ*, the sample can be treated with the concentrated HCl and ethanol only. Neither chromium nor water are added.

Only the acid volatile sulfur fraction will react under these conditions and can thus be selectively analysed. If the total reduced inorganic sulfur is required, the same sample can then be treated with the chromous chloride reductant by introducing chromium powder and water into the reaction chamber as described above.

By way of example only, the present invention will now be described with reference to the Figure which schematically illustrates a preferred apparatus of the present invention.

The apparatus 11 is designed to be fully automated and to be portable to allow onsite use in the field. The apparatus has a removable reaction vessel 12. An operator can place a known volume or mass of a sample to be tested into the reaction vessel. Alternatively, the apparatus can include an in-built balance to measure the mass of material in the reaction chamber. The reaction vessel 12 is placed in a heating mantle 13 which is equipped with a magnetic stirrer. In use, the reaction vessel is connected, with an air-tight seal, to inlets 14, 15 and outlet 16. The sealed connection may

be provided by any suitable means such as ground glass joints or O ring seals.

The inlet 14 is connected to a chromium powder dispenser 17. The inlet 15 is connected, with an air-tight seal, to a nitrogen gas source 18 and to acid, water and ethanol reservoirs 19, 20, 21. The reservoirs 19, 20, 21 each have a peristaltic pump 22, 23, 24 for delivering pre-determined amounts of liquids via three way valves 25 to inlet 15. To the outlet 16 is connected an insulated condenser 26 which typically has copper pipes surrounding a glass core. Refrigerent is supplied to the condenser 26 from pump 27. Typically, the apparatus includes a heat exchange apparatus by which heat extracted from the condenser can be used to heat the mantle 12. The upper end of the condenser 26 is connected, via an air-tight seal, to an IR gas analyser 28. A moisture trap 29 containing a desiccant is disposed between condenser and analyser 28.

The apparatus is operated by a central control computer 30. The power source 31 is typically a 12V power supply.

To operate the apparatus, an operator places an amount of a sample to be tested in the reaction chamber and places the chamber in the mantle. Prior to analysis, the reservoirs of the chamber are charged with chromium powder, ethanol, water and concentrated HCl respectively. The sample to be tested may be any material containing reduced inorganic sulfur and includes soil, mine spoil, fossil fuels such as coal and oil, sediments, plants and animal materials, water (both naturally occurring and waste), chemical waste and minerals. The samples may be pretreated depending on the nature of the sample. For example the mineral samples may be fine ground prior to analysis.

The apparatus is operated by the computer 30 which can be programmed to fully automate the analysis. If desired manual override capabilities may be included. Under normal operational conditions, all that is required

of the operator after placement of the sample in the reaction chamber is to press an "on" switch. This will initiate purging of the system with nitrogen for a pre-determined and monitored flow rate. After a fixed time, pre-determined amounts of chromium powder, water, ethanol and 12N HCl are added to the reaction chamber in turn.

The amounts of reagent added will depend on the weight of the sample. For a 1g sample, typically about 2.059g chromium powder, 10mL ethanol, 28.25mL of 12N HCl and 31.75mL of water are added.

After addition of the reagents, the reaction chamber is heated to boiling with stirring. As  $H_2S$  is evolved it is carried by the nitrogen through the dessicant in the moisture trap 29 to the IR gas analyser 28. The cumulative concentration of the  $H_2S$  gas is calculated by the computer 30 using an algorithm relating  $H_2S$  concentration and nitrogen gas flow rate. When  $H_2S$  evolution has ceased or fallen below a pre-determined level the computer will terminate the analysis by sequentially disengaging the  $H_2S$  IR gas analyser, and turning off the heating mantle 13, gas flow and condenser 26. The reaction vessel 12 can then be removed by the operator and cleaned. The apparatus is ready for the next analysis.

The total amount of reduced inorganic sulfur can be read directly from a digital panel or stored digitally. The results may also be presented graphically as either cumulative  $H_2S$  production or real time  $H_2S$  production rates.

The above procedure may be modified to separately analyse the acid volatile sulfur fraction. In this case, the sample is placed in the reaction chamber as before, but only HCl (20mL) and ethanol (10mL) are added. The heating mantle on the condenser is not required and remains turned off. If both the acid volatile and total reduced sulfur are required, the first procedure may then be performed on the sample remaining in the reaction chamber. However, it will only be

necessary to add 8.25mL of HCl (because 20mL have already been added) plus the chromium powder and water.

It can be seen that the apparatus of the present invention can provide a self contained, portable and automated analyser for reduced inorganic sulfur. At present there is no automated system for quantifying reduced inorganic sulfur. All existing techniques used by industry must be performed by skilled personnel in a well equipped laboratory. Thus, it has hitherto not been possible to analyse reduced inorganic sulfur on site. Automation of the present apparatus allows onsite analysis. Further, skilled laboratory personnel are not required to conduct the analysis.

The present apparatus can be in the form of a completely portable unit which may be operated from a 12V power supply. The present apparatus can also be operated using a mains power supply in the laboratory. The use of a refrigeration system to provide both the heating for the mantle and cooling of the condenser contributes to the ability of the apparatus to be self contained. Such portability and self containment is not possible with conventional wet chemistry techniques.

The ability to constantly monitor  $H_2S$  evolution and to detect when such evolution ceases also offers significant advantages over wet chemical analytical techniques in which a sample is digested for a set period of time. The present inventors have observed that for some samples, digestion can be completed in about 10 minutes as compared to the standard time of one hour allowed for reaction. Thus by monitoring completion of the reaction, the speed of analysis can be considerably increased.

The present invention also provides a method and apparatus for selectively measuring the reduced inorganic sulfur without interference from organic sulfur and sulfate materials. Still further, the acid volatile sulfur fraction can be selectively measured. Also, by monitoring the rate of hydrogen sulfide evolution,

important information can be obtained as to the relative amounts of different types of reduced inorganic sulfur in the sample.

5 It will be appreciated that various changes and modifications may be made to the embodiments as described herein without departing from the spirit and scope of the invention.

DATED this 22nd day of March 1999

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